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POLYMERS FOR SPACECRAFT HARDWARE

Prepared for:

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

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SRI Project ASD-5046

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Analyses and Instrumentation

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SCOPE

This report covers work performed during the period June 10 to July 9, 1966 on "Polymers for Spacecraft Hardware," SRI Project ASD-5046 under JPL Contract No. 950745.

The primary objectives of this program are to assist the Jet Propulsion Laboratory of the California Institute of Technology in the evaluation of polymeric materials to be used in connection with JPL spacecrafts, and to provide a study of the effects of simulated spacecraft environment on selected commercial polymeric products. The materials and products to be studied and the extent of the work to be performed are specified by the JPL Cognizant Engineer.

WORK PERFORMED

Materials Evaluation

Work has been completed on the mixing and curing of polymeric materials selected by the JPL Cognizant Engineer for determination of changes in properties such as dielectric constant, adhesion, compression set, etc. subsequent to exposure to a thermal-vacuum environment of 135°C and $<10^{-5}$ torr for a period of 500 hours. The materials which required mixing and curing are adhesives, sealants, protective coatings, and foams; other polymers to be tested, such as structural materials, gasket materials, lubricants, etc. will require only simple postcures.

Fabrication has been completed for the multiple-cell unit to be used for the thermal-vacuum exposure of the above materials. The system is being assembled for check-out of fittings and welds, refrigeration, and thermal control. Fabrication of holding fixtures for sample materials is underway and preparation of test schedules and data forms is near completion.

Volatile Condensable Material

Macro-VCM

Fabrication, assembly, and preliminary check-out has been completed for the vacuum system and the heated sample chambers which will be used for the determination of the deposition and subsequent evaporation of volatile condensable material with time.

The essential components of the vacuum system are:

1) Cenco Hypervac-100, roughing pump;
2) Welch Model 1401, holding pump;
3) CVC PMCU-10B, 10-inch diffusion pump;
4) Temescal F-2530, vacuum valve;
5) Cold trap, Freon-502, refrigeration.

The vacuum chamber is a 24-inch diameter, 35-inch long cast-steel belljar. As shown in Figure 1, the supporting rack for the VCM apparatuses is fastened to the face-plate of the vacuum chamber, and the belljar is moved into place on a track. Figure 1 also illustrates the partial assembly of the heater units and the supporting electrical and plumbing equipment. The nozzle of each sample chamber is positioned so that volatile material (125°C) will pass through an opening in an aluminum baffle to a polished aluminum VCM collector plate (1-1/2" diameter) maintained at about 25°C by water-cooling lines soldered to the collector-plate support.

The heated sample chambers consist of two spun-copper halves, each wound with an Xactiglo heating element soldered in place. The halves are joined and sealed with (TFE) washers. Individual thermal-control and thermocouple systems are provided for each apparatus (see meters, lower right-hand corner of Figure 1). Design drawings of the sample units will be issued in a summary report.

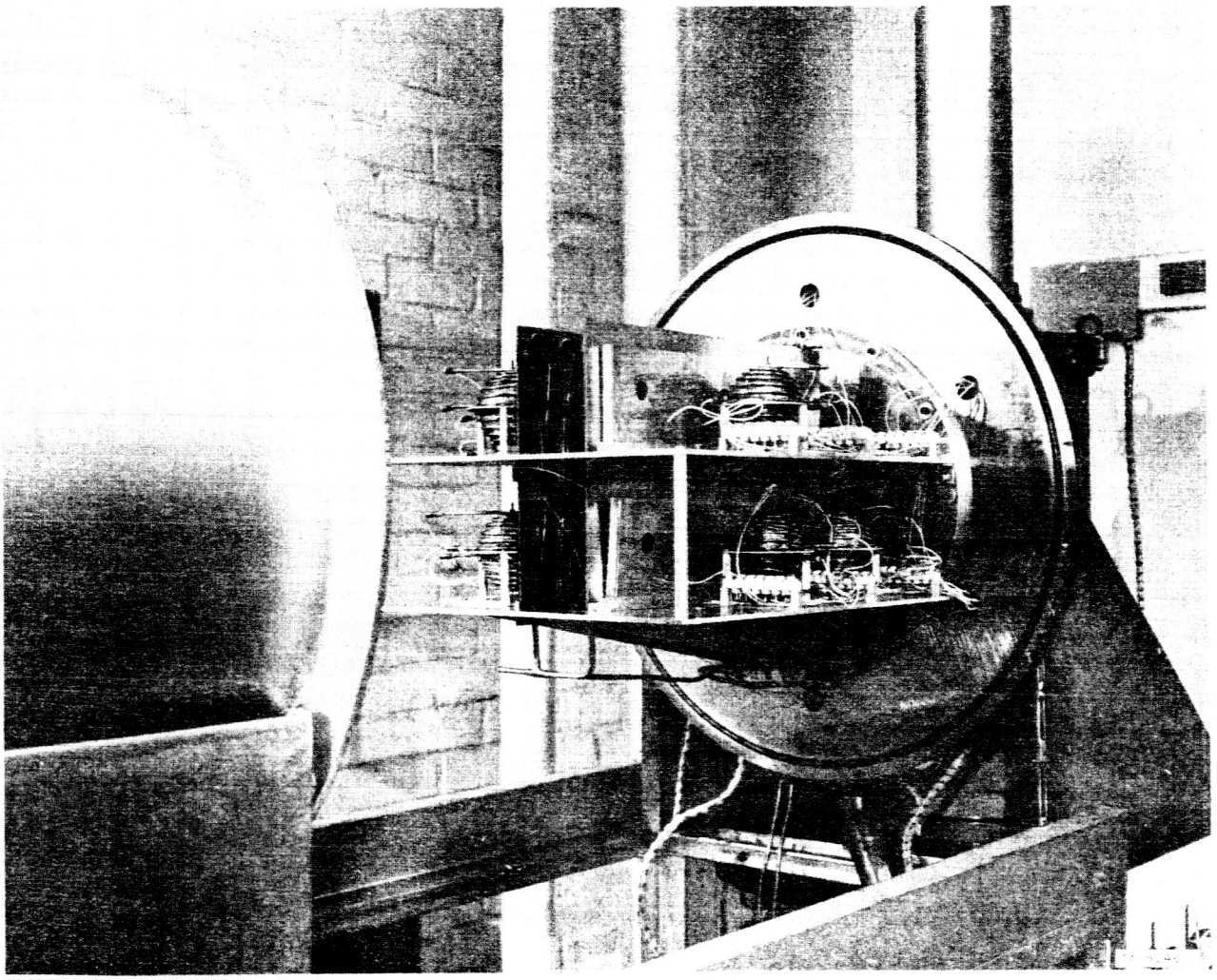

FIG. 1 PHOTOGRAPH OF PARTIAL ASSEMBLY OF VCM APPARATUSES

The initial run for macro-VCM determinations with the "improved" VCM apparatuses has just been started. Five materials are being run in duplicate along with two blanks in diametrically-opposed positions. The materials for this first run were selected for comparison with previously-acquired VCM data, for correlation with past and present data on other properties, and for additional examination of potentially-good spacecraft materials. The information summarized in Table I indicates not only the materials under test but also the continual effort during this program to evaluate a material for spacecraft use on the basis of combined properties and to determine the correlation between the various properties and the significance thereof.

Table I

Macro-VCM Determinations:
Polymeric Materials Under Test and Prior History

Material	Prior Macro-VCM	Micro-VCM	Std. Vac. Wt. Loss	Volatiles Mass Spec	Mech Prop	8-mo. Stg.
Viton A441IA-990 (vinylidene fluoride-hexafluoropropylene elastomer)	X	X	X	X	X	X
Hycar-520-67-108-1 (acrylic elastomer)	-	X	X	X	X	X
SE3604 (silicone elastomer)	-	X	X	X	X	X
PPO (clear) (polyphenylene oxide film)	-	X	X	X	X	X
Teflon FEP 500A (polyfluoroethylene-propylene film)	-	X	X	X	X	X

Micro-VCM

The results of micro-VCM determinations for a number of polymeric materials are summarized in Tables II to V. For the most part, the range of values for weight loss and VCM falls within that experienced for specific polymer classes. The sleeving material understood to be glass fiber only (See Table V) is off-color and appears to be impregnated or coated; confirmation of the presence of a material which is volatile and condensable is being sought by mass spectrometric analysis.

Table II

Micro-VCM Determinations: Adhesives
(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25° C)

Material	Mfr.*	Total Wt. Loss, %	VCM, wt-%	Noncondensable Wt. Loss, %	Notes**
Epoxy					
Eccobond-55/11	EMC	3.76	3.40	0.36	2, 3
Eccobond-55/11	EMC	0.43	0.43	0.00	2, 4
Eccobond-45/15	EMC	0.55	0.05	0.50	2, 5
Silicone					
RTV-41/T-12	GES	2.06	0.45	1.51	2, 6

*EMC, Emerson and Cuming, Inc.
GES, General Electric Company, Silicone Products Department

**2) Conditioned in 50% humidity for 24 hr prior to initial weighing and stored in desiccator for 30 minutes before final weighing.

3) Cured 1/2 hr at 150°C.

4) Cured 24 hr at 150°C.

5) Cured 1/2 hr at 70°C.

6) Cured 8 hr at 25°C and 4 hr at 50°C.

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Table III

Micro-VCM Determinations: Hardware and Structural Materials

(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25° C)

Material	Mfr.*	Total Wt. Loss, %	VCM, wt-%	Noncondensable Wt. Loss, %	Notes**
Polyamide					
Zytel-101-NC-10	DUP	3.58	0.21	3.37	1, 2
Zytel-31	DUP	1.85	0.42	1.43	1, 2
Zytel-42	DUP	2.57	0.26	2.31	1, 2

*E. I. du Pont de Nemours and Company, Plastics Department

**1) As received.
2) Conditioned in 50% humidity for 24 hr prior to initial weighing and stored in desiccator for 30 minutes before final weighing.

Table IV

Micro-VCM Determinations: Honeycomb Core Materials

(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25°C)

Material	Mfr.*	Total Wt. Loss, %	VCM, wt-%	Noncondensable Wt. Loss, %	Notes**
Silicone					
Hexcel HRS-asbestos	HEX	0.37	0.37	0.00	1, 2
Hexcel HRS-glass fiber	HEX	0.50	0.40	0.10	1, 2
Phenolic					
Hexcel HRP	HEX	1.30	0.20	1.10	1, 2
Polyester					
Hexcel HMH	HEX	0.18	0.17	0.01	1, 2

*HEX, Hexcel Products, Inc.

**1) As received.
2) Conditioned in 50% humidity for 24 hr prior to initial weighing and stored in desiccator for 30 minutes prior to final weighing.

Table V

Micro-VCM Determinations: Sleeving

(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25°C)

Material	Mfr. *	Total Wt. Loss, %	VCM wt-%	Noncondensable Wt. Loss, %	Notes**
Glass fiber only (?)					
Ben-Har Ex-Flex 1500	BHM	0.18	0.14	0.04	2, 3
Ben-Har Pyro-Sleeve	BHM	0.13	0.11	0.02	2, 3
Acrylic-glass fiber					
Ben-Har 1258-1. B	BHM	0.56	0.35	0.21	2, 3
Ben-Har 263, G3	BHM	1.40	0.27	1.13	2, 3
Ben-Har Lectron B	BHM	0.09	0.09	0.00	2, 3
Ben-Har Acryl A, BAI	BHM	0.22	0.16	0.06	2, 3
Silicone-glass fiber					
Ben-Har 1151, Armasil GR-2	BHM	0.54	0.42	0.12	2, 3
Ben-Har 1151, UL	BHM	0.66	0.43	0.23	2, 3
Ben-Har 1151, Superwall	BHM	0.31	0.31	0.00	2, 3

*BHM, Bentley-Harris Manufacturing Company

** 2) Conditioned in 50% humidity for 24 hours prior to initial weighing and cooled in desiccator for 30 minutes before final weighing.

3) Postcured 24 hr at 150°C.

Volatile Material

Mass Spectrometry

The mass spectrometric identification *in situ* of substances volatilized from polymeric materials at 125°C has been completed for two samples of interest: (1) Micarta b5M25, a copper-clad epoxy-glass fiber printed-circuit material (a question of corrosive evoluents was raised by the JPL Cognizant Engineer); (2) Teflon-FEP 500A, a polyfluoroethylenepropylene structural film (the deposition of VCM was unexpected). The results of the analyses are given in Table VI; values are given only to indicate relative order of abundances of components in the vapor released under vacuum at 125°C.

Table VI

Mass Spectrometric Analyses *In Situ* of Volatile Materials from Selected Polymers (125°C and 10^{-5} torr)

Polymer Identification	Component	Estimated mol-%
Micarta b5M25 (Westinghouse)	Commerical solvents, e.g., methyl cellosolve	92
	Styrene	7
	Unidentified organics	1
Teflon-FEP 500A (Du Pont)	Phthalic acid ester	42
	~C_{30} unsat'd hydrocarbon	35
	Carbon dioxide	4
	Hydrofluoric acid	1
	Water	18

Mechanical Properties

Six-Week Storage Tests

In situ tests of the effects of the vacuum-thermal environment on the mechanical behavior of elastomers Hycar 520-67-108-4 and Butyl rubber EX-1090, and Mylar film Type 500A, were completed on May 25. In addition, ring specimens of Hycars -4, -5, -6, SE-3704, and SE-3804 as well as dumbbell specimens of Mylar and Bakelite Polysulfone film (P-2300) were stored in the test chamber and were tested at the conclusion of the exposure period. All results are presented below.

Results of continuous and intermittent stress relaxation tests of Hycar-4 and Butyl rubber EX-1090 are shown in Table VII. By comparing these results with previous data [1, 2], it is noted that the behavior of Hycar-4 is approximately comparable to that of Hycar-2, both compositions showing more extensive chain scission than Hycar-1. The relative degree of chain scission effected by 500 hours of exposure to the vacuum-thermal environment for the Hycar elastomers thus far tested, can be portrayed as follows:

$$\text{Hycar-1} < \text{Hycar-2, Hycar-4} \ll \text{Hycar-3}$$

The relative rates of cross-linking, as measured by the difference between continuous and intermittent measurements, can be shown as:

$$\text{Hycar-1} < \text{Hycar-3, Hycar-4} \ll \text{Hycar 2}$$

Butyl rubber EX-1090 was found to behave about like Hycar-1.

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[1] Muraca, R. F., et al., Stanford Research Institute, Interim Report No. 2, Project 5046, March 15, 1966.

[2] Muraca, R. F., et al., Stanford Research Institute, Monthly Technical Progress Report No. 22, Project 5046, April 15, 1966

Examination of the data of Table VIII and comparison with previous data [1, 2], yields confirming information that, of the first four Hycar elastomers, Hycar-1 appears to be the least affected by the vacuum-thermal environment. However, on the basis of the effects on tensile properties shown in Table VIII, Hycar-5 and -6 appear to be superior to Hycar-1. Similarly, comparisons of the measured changes to modulus and rupture strain values indicate the following order of stability to the vacuum-thermal environment for the silicone elastomers:

SE-3604 >SE-3813 > SE-3613, SE-3713 >SE-3704, SE-3804

Table IX summarizes the effects of the vacuum-thermal environment on the tensile properties of Mylar and polysulfone films. The polysulfone film appeared to be only slightly affected by the exposure, with about a 25% increase in modulus and almost no change in rupture properties being observed. The Mylar demonstrated considerable change, in that modulus increased more than two-fold and yield strain decreased by about 50%, although rupture properties (based on single tests) were almost unaffected.

In situ constant load tests of Mylar were conducted with duplicate specimens subjected to loads of 1500 and 2000 psi. All creep deformation occurred within the first 100 hours of exposure to the vacuum-thermal environment; no change was noted thereafter. Total deformation values, based on an effective gage length of 0.8 inch, are shown below:

	Deformation, in/in	
	2000 psi	1500 psi
	.063	.037
	.037	.025
Ave.	.050	.031

The current vacuum-thermal storage program was initiated on June 14, when temperatures were increased to 125°C after conditioning at 50°C for about 170 hours. Materials under investigation are:

(a) Continuous and intermittent stress relaxation
Hycars -5 and -6

(b) Constant loan (duplicate specimens at 7, 500 and 10, 000 psi)
Kapton 200XH667

(c) Storage
Kapton 200XH667 (polyimide film, DuPont)
Tedlar 200SG40TR (polyvinyl fluoride film DuPont)
SE-556 (silicone elastomer, General Electric)

Table VII
Effect of Vacuum-Thermal Environment
on Stress-Relaxation Behavior of
Hycar and Butyl Rubbers

Material	Intermittent			Continuous		
	Approx Time to f (t)/f (o) >1.0 hours	f (t)/f (o) at 20 hrs	500 hrs	Approx Time to f(t)/f (o) = 0.9 hours	f (t)/f (o) at 20 hrs	500 hrs
Hycar-4	5	1.03	1.63	1	0.81	0.69
EX-1090	0.5	1.17	1.60	1	0.83	0.76

Notes: 1. All tests conducted at strains of approximately 0.25

2. Data obtained from best curves drawn through duplicate test results.

3. Exposure conditions consisted on two stages:

(a) 190 hours at 50°C and an average pressure of about 4×10^{-6} torr

(b) 1004 hours at 125°C and an average pressure of about 2.5×10^{-6} torr.

Table VIII

Effect of Vacuum-Thermal Environment
on Tensile Properties of Hycar and Silicone Rubbers

Material	History	Test Temp., °C	Stress at Strain of 0.25, psi	Stress at Rupture, psi	Strain at Rupture, in/in
Hycar-4	Control	25	121	920	1.25
	Exposed	25	243	630	0.49
	Control	125	128	365	0.68
	Exposed	125	260	380	0.35
Hycar-5	Control	25	41	815	2.12
	Exposed	25	60	930	2.14
	Control	125	30	270	1.65
	Exposed	125	45	285	1.15
Hycar-6	Control	25	243	1490	1.24
	Exposed	25	348	1590	1.07
	Control	125	162	800	0.95
	Exposed	125	232	735	0.70
SE-3704	Control	25	180	595	1.52
	Exposed	25	259	600	0.73
	Control	125	199	475	1.10
	Exposed	125	277	515	0.55
SE-3804	Control	25	261	500	1.05
	Exposed	25	394	660	0.59
	Control	125	260	435	0.66
	Exposed	125	383	440	0.42

Notes: 1. All data points are averages of measurements on duplicate specimens.

2. Tests were conducted at an extension rate of 0.1 in./min.

3. Control specimens were stored at normal room conditions for the entire period from specimen preparation to final testing.

4. Exposure conditions consisted of two stages: (a) 190 hours at 50°C and an average pressure of about 4×10^{-6} torr, (b) 1004 hours at 125°C and an average pressure of about 2.5×10^{-6} torr.

Table IX

Tensile Properties of Mylar and Polysulfone

Material	History	Modulus psi	Yield		Rupture	
			Stress psi	Strain in/in	Stress psi	Strain in/in
Mylar	Control	33,000	2990	0.09	12,300	1.74
	Exposed	72,000	4240	0.059	10,700	1.82
Polysulfone	Control	82,000	--	--	4,940	0.085
	Exposed	103,000	--	--	5,040	0.081

Notes: 1. Materials were: Mylar, Type 500A
Bakelite Polysulfone P-2300 annealed for 1 hr. at 165°C

2. All tests were conducted at a cross head rate of 0.02 in/min and at a temperature of 125°C.

3. Test specimens were dumbbell shapes; 0.005-inch thick, 0.125 - inch width, 0.8-inch test length. Strain was calculated on the basis of an 0.8-inch effective gage length.

4. Exposure conditions consisted of two stages: (a) 190 hours at 50°C and an average pressure of about 4×10^{-8} torr, (b) 1004 hours at 125°C and an average pressure of about 2.5×10^{-8} torr.

5. Yield values for Mylar were obtained at the intersection of the modulus line and the tangent to the yielding curve.

6. Rupture data for Mylar are single test values; all other data are average values of four tests.

Eight-Month Storage Tests

During the past month of storage at constant strain in an environment of 125°C and $< 10^{-8}$ torr, no samples have ruptured; elastomers being examined are General Electric SE-3604 (silicone), Du Pont Viton A4411A-990 (vinylidene fluoride-hexafluoropropylene), and Goodrich Hycar-1 (polyacrylic). As of this reporting period, 6-1/2 months of storage have been completed; five samples ruptured during outgassing at 40°C (SE-3604 and Viton A4411A-990 at maximum strain) and 3 samples ruptured during the first week at 125°C (Hycar-1 at maximum strain).

Long-term constant-load tests of polyphenylene oxide film in the thermal-vacuum environment have now been in progress for 4 months. The PPO specimens (General Electric) have shown almost negligible creep during this period; however, one specimen at 1750 psi ruptured during the third month.

FUTURE WORK

Materials Evaluation

It is anticipated that the fabrication of holding fixtures will be completed and the first run will be initiated during the next working period.

Volatile Condensable Material

Micro-VCM determinations will be continued on a routine basis. It is anticipated that no difficulties will be encountered with the macro-VCM apparatus and that runs will be made on a continuing basis.

Volatile Material

Work is coninuing on the mass spectrometer analyses of substances released from polymeric materials at 125°C in vacuo.

Mechanical Properties

Work will continue on the measurements of stree-relaxation changes for selected polymer during a 6-week exposure to the thermal-vacuum environment of 125°C and 10^{-6} torr.

Regular observations will be made of the status of the elastomers which are stored in the thermal-vacuum environment under constant strain for 8 months and of the plastic which is being stored under constant load for 6 months.